

# PATENT SPECIFICATION (11)

1424382

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 (31) Convention Application No. 7366/72 (32) Filed 18 Jan. 1972 in  
 (33) Japan (JA)  
 (44) Complete Specification Published 11 Feb. 1976  
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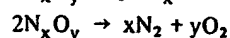
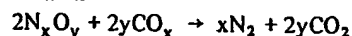
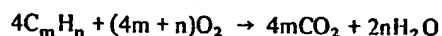
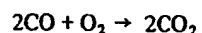


## (54) A CATALYTIC COMPOSITION CONTAINING PALLADIUM AND CHROMIUM OXIDES

(71) We, NISSAN MOTOR COMPANY LIMITED, a corporation organized under the laws of Japan, of No. 2, Takaramachi, Kanagawa-ku, Yokohama City, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

This invention relates to a catalytic composition for the treatment of exhaust gases containing hydrocarbons, carbon monoxide and nitrogen oxides.

It has become a matter of great concern to remove air pollutants from the automotive and various industrial exhaust gases before they are released to the open air. The exhaust gases usually contain noxious compounds such as hydrocarbons and carbon monoxide resulting from partial or incomplete combustion of hydrocarbon fuels, and nitrogen oxides produced by the reaction between oxygen and nitrogen gases in the air used for the combustion of the fuels at elevated temperatures. Emission in untreated condition of these gases imposes a serious problem of air pollution. From a viewpoint of preventing this undesirable air pollution caused by the emission of these noxious compounds, it is strongly desired to render the exhaust gases harmless by oxidizing carbon monoxide and hydrocarbons in the exhaust gases and by reducing or decomposing the nitrogen oxides before the exhaust gases are released. Various types of catalytic compositions have been proposed hereinbefore in an attempt to convert the noxious exhaust gas components into harmless compounds. Conversions of the harmful components are carried out through chemical reactions expressed by the following formulae:



where  $m$ ,  $n$ ,  $x$  and  $y$  are, respectively, integers which are determined appropriately.

A catalytic composition used to accomplish these purposes, particularly in internal combustion engines of motor vehicles, should meet the following requirements:

- (1) Prolonged active life showing optimum reactivity for oxidation or reduction of the respective noxious compounds over as long a period of time as possible.
  - (2) Low-temperature activity, viz., capability of being active at relatively low temperatures.
  - (3) Satisfactory conversion efficiency for oxidizing combustible compounds and reducing nitrogen oxides contained in the exhaust gases within a temperature range of 100°C to 900°C.
  - (4) Sufficient mechanical strength, in particular resistance to attrition and to mechanical shocks, oscillations and vibrations while in operation.
  - (5) Low resistance to the flow of exhaust gases through the catalytic composition.
- Of these, the requirements (2), (4) and (5) will not be satisfactorily met by known catalytic compositions in the form of spheres, pellets or tablets. However, the requirements are all met by a composition in the form of a black having a volume equivalent to from several

PATENTS ACT 1949

SPECIFICATION NO 1424382

Reference has been directed, in pursuance of Section 8, of the Patents Act 1949, to Specification No 1403555.

THE PATENT OFFICE  
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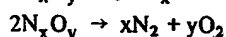
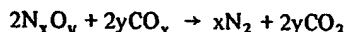
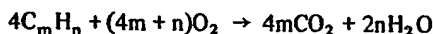
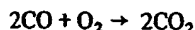


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A catalytic composition used to accomplish these purposes, particularly in internal combustion engines of motor vehicles, should meet the following requirements:

(1) Prolonged active life showing optimum reactivity for oxidation or reduction of the respective noxious compounds over as long a period of time as possible.

(2) Low-temperature activity, viz., capability of being active at relatively low temperatures.

(3) Satisfactory conversion efficiency for oxidizing combustible compounds and reducing nitrogen oxides contained in the exhaust gases within a temperature range of 100°C to 900°C.

(4) Sufficient mechanical strength, in particular resistance to attrition and to mechanical shocks, oscillations and vibrations while in operation.

(5) Low resistance to the flow of exhaust gases through the catalytic composition.

Of these, the requirements (2), (4) and (5) will not be satisfactorily met by known catalytic compositions in the form of spheres, pellets or tablets. However, the requirements are all met by a catalytic composition in the form of a lump or block having a volume equivalent to from several tenths of a liter to several liters and having therein a number of through-passages extending in one or two directions. Such a catalytic composition is generally called a "monolithic or block catalytic composition" and will be herein referred to as such. The monolithic catalytic composition structure has typically a honeycomb-like or a sieve-like cross section. In contrast to such a

monolithic catalytic composition, the catalytic composition in the sphere, pellet or tablet form will be called herein a "non-monolithic catalytic composition". The monolithic catalytic composition is considered suitable for use particularly in treatment of automotive exhaust gases although the non-monolithic catalytic composition is acceptable for use in the treatment of exhaust gases from industrial power plants and automotive internal combustion engines as well.

The monolithic catalytic composition may be prepared by any of the following three different methods:

i) A mixture of catalytic agents and a carrier material is first prepared by mixing or by precipitation. The mixture is then moulded into a specific monolithic form and sintered to produce a monolithic catalytic composition.

ii) Catalytic agents are precipitated on a previously moulded monolithic carrier structure by a suitable method and then sintered to form a monolithic catalytic composition.

iii) A previously moulded monolithic carrier structure is impregnated with a solution of salts or other compounds of catalytic components, and then the resultant carrier is sintered to give a monolithic catalytic composition.

"The catalytic carrier" mentioned above is intended to define a carrier having a specific structure similar to that of the monolithic catalytic composition defined hereinbefore.

Of the three different methods mentioned above, the methods (i) and (ii) involve various technical problems to be solved and thus are unacceptable for practical applications. However, the method (iii) is easy to carry out and suitable for use in the production of a monolithic catalytic composition which is sufficiently active and durable.

A variety of catalytic agents are presently available for the purpose of removing noxious compounds from the exhaust gases emitted from the automotive internal combustion engines, including: (a) a catalytic agent containing copper oxide with or without the following: manganese oxide, chromium oxide and/or magnesia, (b) a catalytic agent containing manganese oxide and/or iron oxide, (c) a catalytic agent containing nickel oxide and chromium oxide with or without barium oxide, and (d) palladium and copper oxide and at least one of the following: chromium oxide, manganese oxide and magnesia. These catalytic agents, however, are not fully acceptable because the catalytic agent (a) has a disadvantageously short active or durable life because of the copper oxide contained therein, though excellent in low-temperature activity, and the catalytic agent (b) mainly composed of manganese oxide is poor in its low-temperature activity when used in gases containing therein a large amount of moisture as in exhaust gases of industrial power plants or automotive internal combustion engines. Moreover, the catalytic agent (c) is also disadvantageously deficient in low-temperature activity and the catalytic agent (d) has a disadvantageously short active life as well because of the copper oxide contained therein.

According to the present invention, there is provided a catalytic composition for treating exhaust gases containing carbon monoxide, hydrocarbons and nitrogen oxides, said catalyst composition comprising a carrier and palladium and chromium each being in oxide form, the palladium and chromium being supported by the carrier, the palladium being present in an amount of 0.0003 to 0.1 gram atoms per litre of carrier, the chromium being present in an amount of 0.5 to 3.0 gram atoms per litre of carrier, and the composition being free from copper oxide, the composition further comprising at least one further oxide having catalytic activity and selected from barium magnesium, strontium, zirconium, bismuth, vanadium and aluminium oxides, the total amount in gram atoms of the metal or metals of said at least further oxide being within the range of 1/50 to 1/2 of the amount in gram atoms of the chromium.

Research and development work has been carried out by the present inventors to find a catalytic composition which has sufficient activity at low temperatures and which provides a long life of catalytic activity when used under severe conditions as in the exhaust system of a motor vehicle. As a result of such research and development efforts, it has been found that a catalytic composition in accordance with the invention shows satisfactory low-temperature activity and sufficient durability of long life of activity when used for removing air-contaminants from exhaust gases of, particularly, automotive internal combustion engines. The reasons for the increased low-temperature activity and durability of the catalytic composition cannot be fully explained at this stage of research and development. However, these are considered to be due to the following reasons. Palladium oxide contained in the composition has a high low-temperature activity on carbon monoxide and various hydrocarbons and is most excellent in durability. Chromium oxides which may occur in various oxide forms are considerably active on hydrocarbons. Furthermore, copper oxides are not contained in the catalytic composition, so that the activity of the catalytic composition is maintained over a long period of time.

In this Specification, when we refer to the volume of the carrier, we mean the total volume including the volume of internal voids if the carrier is monolithic and we mean the total volume including the voids between particles if the carrier is non-monolithic.

The concentration ranges of the palladium and chromium specified above are determined as a result of the following observations. If palladium in the oxide form is deposited on 1 liter of a carrier in an amount less than 0.0003 gram atoms, the resultant catalytic composition fails to be

active on air-pollutants, particularly carbon monoxide, and thus the amount of palladium should be greater than 0.0003 gram atoms per liter of a carrier. However, in practical applications, the amount of palladium in the form of oxide must be less than 0.1 gram atoms per 1 liter of a carrier mainly for economic reasons. Unless chromium oxide is deposited on 1 liter of a carrier in an amount over 0.05 moles as metal, the chromium oxide is hardly effective for conversion of air-pollutants. If the amount of chromium in the oxide form is more than 3.0 gram atoms per liter of the carrier, then not only is the activity of the catalytic composition low presumably because of low surface area of the chromium oxide, but also the chromium oxide incompletely adheres to the carrier and tends to be entrained in the stream of exhaust gases and discharged into the open air, causing heavy metal contamination of the air. Thus, the concentration of the chromium in the form of chromium oxide must be within the range of 0.05 – 3.0 gram atoms per liter of a carrier.

As a result of a series of extensive studies for further improving the activity and durability of the catalytic composition in accordance with the present invention, it has been found that the low-temperature activity and durability or stability of the catalytic composition is markedly improved by the presence of the one or more of oxides selected from oxides of barium, magnesium and strontium. Furthermore, the presence of the at least one oxide having catalytic activity and selected from oxides of zirconium, bismuth, vanadium and aluminium is found to improve the durability of the composition. The reason for such improvement in activity and durability or stability by the incorporation of the above-mentioned compounds into the composition is not known at present.

The total amount in gram atoms of the metal or metals of said at least one oxide selected from oxides of barium, magnesium, strontium, zirconium, bismuth, vanadium and aluminium is  $1/50 - 1/2$  of the amount in gram atoms of the chromium of the chromium oxide. The total amount in gram atoms of the above-mentioned oxide or oxides may be varied within the range mentioned irrespective of the number and types of the oxides selected. If, however, the oxides are used in a concentration below the lower limit specified, the intended effects of the oxides, i.e. the improvements in durability and activity of the catalytic composition obtained, are not achieved. If the concentration of the oxide or oxides is higher than the upper limit specified above, the activity of the catalytic composition is decreased.

The carrier for use in the catalytic composition according to the present invention may be of alumina, silica-magnesia or baked clay. The carrier may be monolithic or non-monolithic. The monolithic carrier may be formed from a material containing alumina such as cordierite, beta-spondumene or alpha-alumina. The non-monolithic carrier such as in the form of spheres, pellets or tablets may be formed from a material containing alumina such as alpha-alumina, gamma-alumina, delta-alumina or chi-alumina. If desired, the monolithic carrier formed of cordierite, beta-spondumene or alpha-alumina may be improved by coating an activated alumina such as gamma-alumina or kappa-alumina on the surface of the base material. The carrier of this particular type will be hereinafter referred to as an "alumina-coated monolithic carrier" or a coated carrier for convenience.

Methods of preparing the catalytic composition of the present invention are described hereinafter. One of the methods comprises: forming a carrier in suitable form; immersing the carrier in a solution of water-soluble compounds or salts of palladium and chromium; and thereafter sintering the carrier at a temperature of  $600 - 900^{\circ}\text{C}$ . The water-soluble compound or salt of palladium may be palladium nitrate, palladium bromide, palladium chloride or palladium sulfate, and those of chromium may be chromium nitrate, chromium acetate, ammonium dichromate, ammonium chromate or chromium trioxide. Further, at least one salt or other compound of barium, magnesium, strontium, zirconium, bismuth, vanadium and aluminium must be incorporated in the solution. Barium nitrate, barium acetate, barium formate, barium chloride, barium bromide or barium iodide may be used as a barium salt; magnesium nitrate, magnesium acetate, magnesium chloride, magnesium bromide or magnesium iodide as a magnesium salt; strontium nitrate, strontium chloride, strontium bromide or strontium iodide as a strontium salt; zirconyl nitrate, zirconium nitrate, zirconium chloride or zirconium iodide as a zirconium salt; bismuth nitrate, bismuth chloride or bismuth bromide as a bismuth salt; bismuth oxide may be used instead of the bismuth salt; vanadium chloride or vanadium bromide as a vanadium salt, vanadium oxide may be used instead of the vanadium salt; and aluminium nitrate, aluminium acetate, aluminium chloride, aluminium bromide or aluminium iodide as an aluminium salt.

Another method of the present invention comprises: mixing chromium hydroxide powder and palladium hydroxide powder prepared by a precipitation method, and activated alumina powder and alumina sol; moulding the resultant mixture into a suitable form; and sintering the moulding. At least one hydroxide selected from hydroxides of barium, magnesium, strontium, zirconium, bismuth and vanadium is incorporated in the mixture before moulding to improve the properties of the catalyst composition, particularly activity and durability.

Still another method of preparation of the catalytic composition in accordance with the present invention comprises mixing chromium hydroxide powder, activated alumina and alumina sol; moulding the mixture into a suitable form; immersing the moulding into a solution of a palladium

salt; drying and subsequently intering the resultant moulding at a temperature of 600 to 900°C. It should be noted that any one of the palladium salts mentioned hereinbefore may be applied in this method. Furthermore, at least one hydroxide selected from hydroxides of barium, magnesium, strontium, zirconium, bismuth, and vanadium must be incorporated in the mixture before moulding for the same reason as described above.

The present invention will be more exactly understood from the following examples of the invention and through comparison between these examples and comparative examples, Comparative Examples 1 to 7 being directed to prior art catalytic components and specimens obtained from Comparative Examples 8 to 12 having the same components as in the present invention but not falling within the ranges of this invention. The accompanying drawing illustrates a graph indicating the relationship between the conversion efficiency (to be defined later) of carbon monoxide, propane and nitrogen monoxide and temperatures of a catalyst bed used.

#### Example 1

A 0.785 litres cordierite block carrier was immersed in 3.0 litres of an aqueous solution of a mixture of palladium nitrate, chromium nitrate and barium nitrate wherein the concentrations of palladium ions, chromium ions and barium ions were 0.77 gram ions, 0.50 gram ions and 0.10 gram ions, respectively, per liter of the solution. The thus immersed carrier was removed from the solution, dried at a temperature of 120°C, and then sintered in a stream of air at a temperature of 800°C for 4 hours. The resultant monolithic block catalytic composition contained 0.015 gram atoms of palladium, 0.10 gram atoms of chromium and 0.02 gram atoms of barium, all in oxide form.

#### Example 2

A 0.785 liter beta-spodumene monolithic block carrier was immersed in a commercially available alumina sol. Then, the immersed carrier was removed and sintered at 700°C for 3 hours to deposit thereon gamma-alumina. The same process was repeated two times so that the monolithic carrier was finally coated with a total of 23% by weight of gamma-alumina. The alumina-coated monolithic carrier thus obtained was immersed in 3.0 liters of an aqueous solution of a mixture of palladium nitrate, chromium nitrate and barium nitrate wherein the concentrations of palladium ions, chromium ions and barium ions were 0.020 gram ions, 0.64 gram ions and 0.043 gram ions, respectively, per liter of the solution. The thus treated carrier was removed from the solution, dried at 120°C for 15 hours and sintered in a stream of air at 750°C for 6 hours.

The resultant alumina-deposited monolithic block catalytic composition contained 0.005 gram atoms of palladium, 0.15 gram atoms of chromium and 0.01 gram atoms of barium, all in oxide form.

#### Example 3

1 liter of a commercially available 6 to 8 mesh (Tyler Standard screen mesh) activated non-monolithic alumina (gamma-alumina) carrier was immersed in 1.35 liters of an aqueous solution of a mixture of palladium nitrate, chromium nitrate, and barium nitrate wherein the concentration of palladium ions, chromium ions and barium ions were 0.022 gram ions, 1.10 gram ions and 0.22 gram ions, respectively, per liter of the solution. The thus immersed carrier was removed from the solution, dried at 120°C for 15 hours and then sintered in a stream of air at 750°C for 5 hours. The resultant non-monolithic catalytic composition contained 0.010 gram atoms of palladium, 0.50 gram atoms of chromium and 0.10 gram atoms of barium in 1 liter of the catalytic composition, all in oxide form.

#### Example 4

Example 2 was repeated except that a 0.785 liter cordierite monolithic block carrier was immersed in a commercially available alumina sol. Then, the immersed carrier was removed and sintered at 700°C for 3 hours to deposit thereon gamma-alumina. The same process was repeated two times so that the monolithic carrier was finally coated with a total of 21% by weight of gamma-alumina. The alumina-coated monolithic carrier thus obtained was immersed in 3.0 liters of an aqueous solution of a mixture of palladium nitrate, chromium nitrate and magnesium nitrate wherein the concentrations of palladium ions, chromium ions and magnesium ions were 0.018 gram ions, 0.29 gram ions and 0.0036 gram ions, respectively, per liter of the solution.

The resultant block catalytic composition contained, deposited on the carrier, 0.005 gram atoms of palladium, 0.08 gram atoms of chromium and 0.001 gram atoms of magnesium, all in oxide form.

#### Example 5

Example 3 was repeated except that 1 liter of a commercially available 6 to 8 mesh (Tyler Standard screen mesh) activated non-monolithic alumina (chi-alumina) carrier was immersed in 1.50 liters of an aqueous solution of a mixture of palladium nitrate, chromium nitrate and magnesium nitrate wherein the concentrations of palladium ions, chromium ions and magnesium ions were 0.20 gram ions, 2.0 gram ions and 0.20 gram ions, respectively, per litre of the solution.

The resultant non-monolithic catalytic composition contained 0.010 gram atoms of palladium, 1.0 gram atoms of chromium and 0.10 gram atoms of magnesium and 1 liter of the catalytic composition, all in oxide form.

*Example 6*

Example 1 was repeated except that a 0.785 liter beta-spodumene monolithic block carrier was immersed in 3.0 liters of an aqueous solution of a mixture of palladium nitrate, chromium nitrate and strontium nitrate wherein the concentrations of palladium ions, chromium ions and strontium ions were 0.096 gram ions, 1.30 gram ions and 0.064 gram ions, respectively, per liter of the solution.

The resultant monolithic block catalytic composition contained therein 0.015 gram atoms of palladium, 0.20 gram atoms of chromium and 0.01 gram atoms of strontium, each in an oxide form.

*Example 7*

Example 2 was repeated except that a block of a similar alumina coated monolithic carrier to that used in Example 4 was immersed in 3.0 liters of an aqueous solution of a mixture of palladium nitrate, chromium nitrate and strontium nitrate wherein the concentrations of palladium ions, chromium ions and strontium ions were 0.018 gram ions, 2.9 gram ions and 0.11 gram ions, respectively, per liter of the solution.

The resultant block catalytic composition contained 0.005 gram atoms of palladium, 0.80 gram atoms of chromium and 0.03 gram atoms of strontium in oxide form.

*Example 8*

Example 1 was repeated except that a block of a similar monolithic carrier to that used in Example 6 was immersed in 3 liters of an aqueous solution of a mixture of palladium nitrate, chromium nitrate, barium nitrate and magnesium nitrate wherein the concentrations of palladium ions, chromium ions, barium ions and magnesium ions were 0.13 gram ions, 1.30 gram ions, 0.13 gram ions and 0.13 gram ions respectively, per liter of the solution.

The resultant block catalytic composition contained therein 0.020 gram atoms of palladium, 0.20 gram atoms of chromium, 0.020 gram atoms of barium and 0.020 gram atoms of magnesium, each in an oxide form.

*Example 9*

Example 2 was repeated except that a block of a similar alumina-coated monolithic carrier as used in Example 4 was immersed in 3.0 liters of an aqueous solution of a mixture of palladium nitrate, chromium nitrate, barium nitrate and strontium nitrate wherein the concentrations of palladium ions, chromium ions, barium ions and strontium ions were 0.029 gram ions, 0.55 gram ions, 0.18 gram ions and 0.0036 gram ions, respectively, per liter of the solution.

The resultant monolithic block catalytic composition contained 0.008 gram atoms of palladium, 0.15 gram atoms of chromium, 0.05 gram atoms of barium and 0.001 gram atoms of strontium, each in oxide form.

*Example 10*

Example 3 was repeated except that 1 liter of a similar non-monolithic carrier to that used in Example 3 was immersed in 1.35 liters of an aqueous solution of a mixture of palladium nitrate, chromium nitrate, magnesium nitrate and strontium nitrate wherein the concentrations of palladium ions, chromium ions, magnesium ions and strontium ions were 0.022 gram ions, 1.10 gram ions, 0.022 gram ions and 0.022 gram ions, respectively, per liter of the solution.

The resultant catalytic composition contained metal oxides in which 0.010 gram atoms of palladium, 0.50 gram atoms of chromium, 0.01 gram atoms of magnesium and 0.01 gram atoms of strontium were present in 1 liter of the catalytic composition.

*Example 11*

Alkali-free hydroxides in the form of dried powder prepared by a precipitation method, viz. 1.50 gram atoms of chromium in the form of chromium hydroxide and 0.10 gram atoms of barium in the form of barium hydroxide, and 1 liter of activated alumina powder (200 - 250 mesh Tyler standard screen mesh) were mixed well in a mortar, 0.5 liters of alumina sol containing 10% by weight of alumina were added to the mixture and water was further added to the mixture to give a suitable consistency thereto. Then, the resultant mixture was moulded into 3 x 3 mm tablets by means of a compression type tableting machine. The thus moulded tablets were dried at 120°C for 15 hours and were then immersed in 1 liter of an aqueous solution containing 0.02 gram atoms of palladium in the form of palladium nitrate. The thus immersed tablets were removed from the solution, dried at 120°C for 15 hours and sintered in a stream of air at 700°C for 8 hours to obtain catalytic tablets having, as catalytic components, oxides of chromium, barium and palladium.

*Example 12*

Alkali-free hydroxides in the form of dried powder prepared by a precipitation method, viz., 0.30 gram atoms of chromium in the form of chromium hydroxide and 0.005 gram atoms of magnesium in the form of magnesium hydroxide, and 1 liter of activated alumina powder (200 - 250 mesh Tyler Standard screen mesh) were mixed well in a mortar. 0.5 liters of alumina sol containing 10% by weight of alumina were added to the mixture and water was further added to the mixture to give a suitable consistency thereto. The resultant mixture was moulded into 3 x 3 mm tablets by means of a compression type tableting machine. The thus moulded tablets were

dried at 120°C for 15 hours and then immersed in 1 liter of an aqueous solution containing 0.01 gram atoms of palladium in the form of palladium nitrate. The thus immersed tablets were removed from the solution, dried at 120°C for 15 hours and sintered in a stream of air at 700°C for 8 hours to give catalytic tablets having, as catalytic components, oxides of chromium, magnesium and palladium.

*Example 13*

Alkali-free hydroxides in the form of dried powder prepared by a precipitation method, viz., 0.50 gram atoms of chromium in the form of chromium hydroxide, 0.04 gram atoms of strontium in the form of strontium hydroxide and 0.010 gram atoms of palladium in the form of palladium hydroxide, were mixed well in a mortar. To the mixture were added 1 liter of activated alumina powder (200 - 250 mesh per inch) and 0.5 liters of alumina sol containing 10% by weight of alumina, and water was further added to the mixture to give a suitable consistency thereto. The resultant mixture was moulded into 3 x 3 mm tablets by means of a compression type tableting machine. The thus moulded tablets were dried at 120°C for 15 hours and sintered in a stream of air at 700°C for 8 hours to give catalytic tablets having, as catalytic components, oxides of chromium, strontium and palladium.

*Example 14*

Alkali-free hydroxides in the form of powder prepared by a precipitation method, viz., 0.20 gram atoms of chromium in the form of chromium hydroxide, 0.01 gram atoms of barium in the form of barium hydroxide and 0.005 gram atoms of magnesium in the form of magnesium hydroxide, and 1 liter of activated alumina powder (200 - 250 mesh (Tyler Standard screen mesh) were mixed well in a mortar. 0.5 liters of alumina sol containing 10% by weight of alumina were added to the mixture and water was further added to the mixture to give a suitable consistency thereto. The resultant mixture was moulded into 3 x 3 mm tablets by means of a compression type tableting machine. The thus moulded tablets were dried at 120°C for 15 hours and immersed in 1 liter of an aqueous solution containing 0.02 gram atoms of palladium in the form of palladium nitrate. The tablets thus immersed were removed from the solution, dried at 120°C for 15 hours and sintered in a stream of air at 700°C for 8 hours to give catalytic tablets having, as catalytic components, oxides of chromium, barium, magnesium and palladium.

*Example 15*

Alkali-free hydroxides in the form of dried powder prepared by a precipitation method, viz., 0.80 gram atoms of chromium in the form of chromium hydroxide, 0.04 gram atoms of barium in the form of barium hydroxide, 0.02 atoms of strontium in the form of strontium hydroxide and 0.015 gram atoms of palladium in the form of palladium hydroxide, were mixed well in a mortar. To the mixture were added 1 liter of activated alumina powder (200 - 250 mesh (Tyler Standard screen mesh) and 0.5 liters of alumina sol containing 10% by weight of alumina, and water was further added to the mixture to give a suitable consistency thereto. The resultant mixture was moulded into 3 x 3 mm tablets by means of a compression type tableting machine. The tablets were dried at 120°C for 15 hours and sintered in a stream of air at 700°C for 8 hours to give catalytic tablets having, as catalytic components, oxides of chromium, barium, strontium and palladium.

*Example 16*

Example 1 was repeated except that a block of a similar monolithic carrier to that used in Example 1 was immersed in 3.0 liters of an aqueous solution of a mixture of palladium nitrate, chromium nitrate and zirconyl nitrate wherein the concentrations of palladium ions, chromium ions and zirconium ions were 0.077 gram ions, 1.00 gram ions and 0.15 gram ions respectively, per liter of the solution. The resultant monolithic block catalyst composition contained 0.015 gram atoms of palladium, 0.20 gram atoms of chromium and 0.03 gram atoms of zirconium, all in oxide form.

*Example 17*

Example 2 was repeated except that a block of a similar alumina-coated monolithic carrier to that used in Example 4 was immersed in 3.0 liters of an aqueous solution of a mixture of palladium nitrate, chromium nitrate and zirconyl nitrate wherein the concentrations of palladium ions, chromium ions and zirconium ions were 0.036 gram ions, 0.80 gram ions and 0.26 gram ions, respectively, per liter of the solution.

The resultant block catalytic composition contained 0.010 gram atoms of palladium, 0.50 gram atoms of chromium and 0.07 gram atoms of zirconium, all in oxide form.

*Example 18*

Example 3 was repeated except that 1 litre of a commercially available activated non-monolithic alumina carrier (extrusion moulded product made of delta-alumina and having a diameter of 3 mm) was immersed in 1.20 liters of an aqueous solution of a mixture of palladium nitrate, chromium nitrate and bismuth nitrate wherein the concentrations of palladium ions, chromium ions, and bismuth were 0.022 gram ions, 0.44 gram ions, and 0.022 gram ions, respectively, per liter of the solution.

The resultant catalytic composition contained 0.010 gram atoms of palladium, 0.20 gram atoms

of chromium and 0.01 gram atoms of bismuth in 1 liter of the catalyst composition, all in oxide form.

*Example 19*

Example 1 was repeated except that a block of a monolithic carrier similar to that used in Example 6 was immersed in 3 liters of an aqueous solution of a mixture of palladium nitrate, chromium nitrate and vanadium trioxide wherein the concentrations of palladium ions, chromium ions and vanadium ions were 0.064 gram ions, 2.2 gram ions and 0.064 gram ions respectively, per liter of the solution.

The resultant monolithic block catalytic composition contained, 0.10 gram atoms of palladium, 0.35 gram atoms of chromium and 0.01 gram atoms of vanadium, all in oxide form.

*Example 20*

Example 2 was repeated except that a block of a similar alumina-coated monolithic carrier to that used in Example 2 was immersed in 3.0 liters of an aqueous solution of a mixture of palladium nitrate, chromium nitrate and aluminium nitrate wherein the concentrations of palladium ions, chromium ions and aluminium ions were 0.064 gram ions, 1.30 gram ions and 0.32 gram ions respectively, per liter of the solution.

The resultant block catalytic composition contained derived from the aqueous solution, 0.015 gram atoms of palladium, 0.30 gram atoms of chromium and 0.05 gram atoms of aluminium, all in oxide form.

*Example 21*

Example 3 was repeated except that 1 liter of a similar carrier to that used in Example 3 was immersed in 3.0 liters of an aqueous solution of a mixture of palladium nitrate, chromium nitrate and aluminium nitrate wherein the concentrations of palladium ions, chromium ions, and aluminium ions were 0.022 gram ions, 1.60 gram ions and 0.22 gram ions, respectively, per liter of the solution.

The resultant catalytic composition contained, derived from the aqueous solution, 0.010-gram atoms of palladium, 0.70 gram atoms of chromium and 0.10 gram atoms of aluminium, all in oxide form, in 1 liter of the catalyst.

*Example 22*

Example 2 was repeated except that a block of a similar alumina-coated monolithic carrier to that used in Example 4 was immersed in 3.0 liters of an aqueous solution of a mixture of palladium nitrate, chromium nitrate, zirconyl nitrate and bismuth nitrate wherein the concentrations of palladium ions, chromium ions, zirconium ions and bismuth ions were 0.036 gram ions, 1.50 gram ions, 0.18 gram ions and 0.036 gram ions respectively, per liter of the solution.

The resultant monolithic block catalytic composition contained, 0.010 gram atoms of palladium, 0.40 gram atoms of chromium, 0.50 gram atoms of zirconium and 0.01 gram atoms of bismuth, all in oxide form.

*Example 23*

Example 2 was repeated except that a block of a similar alumina-coated monolithic carrier to that used in Example 2 was immersed in 3.0 liters of an aqueous solution of a mixture of palladium nitrate, chromium nitrate, zirconyl nitrate and aluminium nitrate wherein the concentrations of palladium ions, chromium ions, zirconium ions and aluminium ions were 0.042 gram ions, 2.1 gram ions, 0.042 gram ions and 0.21 gram ions, respectively, per liter of the solution.

The resultant block catalytic composition contained, derived from the aqueous solution, 0.010 gram atoms of palladium, 0.50 gram atoms of chromium, 0.01 gram atoms of zirconium and 0.05 gram atoms of aluminium, all in oxide form.

*Example 24*

Example 1 was repeated except that a block of a similar monolithic carrier to that used in Example 1 was immersed in 3.0 liters of an aqueous solution of a mixture of palladium nitrate, chromium nitrate, bismuth nitrate and vanadium trioxide wherein the concentrations of palladium ions, chromium ions, bismuth ions and vanadium ions were 0.051 gram ions, 1.50 gram ions, 0.10 gram ions and 0.10 gram ions, respectively, per liter of the solution.

The resultant block catalytic composition contained, 0.010 gram atoms of palladium, 0.30 gram atoms of chromium, 0.20 gram atoms of bismuth and 0.02 gram atoms of vanadium, all in oxide form.

*Example 25*

Alkali-free hydroxides in the form of dried powder prepared by a precipitation method, viz., 1.20 gram atoms of chromium in the form of chromium hydroxide and 0.08 gram atoms of zirconium in the form of zirconium hydroxide, and 1 liter of activated alumina powder (200 - 250 mesh (Tyler Standard screen mesh) were mixed well in a mortar. 0.5 liters of alumina sol containing 10% by weight of alumina were added to the mixture and water was further added to the mixture to give a suitable consistency thereto. The resultant mixture was moulded into 3 x 3 mm tablets by means of a compression type tableting machine. The thus moulded tablets were immersed in 1 liter of an aqueous solution containing 0.02 gram atoms of palladium in the form of



palladium nitrate. The tablets were removed from the solution, dried at 120°C for 15 hours, and sintered in a stream of air at 700°C for 8 hours to give catalytic tablets having, as catalytic components, oxides of chromium, zirconium and palladium.

*Example 26*

5 Alkali-free hydroxides in the form of dried powder prepared by a precipitation method, viz., 5  
0.50 gram atoms of chromium in the form of chromium hydroxide and 0.20 gram atoms of  
vanadium in the form of vanadium hydroxide, and 1 liter of activated alumina powder (200 - 250  
10 mesh (Tyler Standard screen mesh) were mixed well in a mortar. 0.5 liters of alumina sol  
containing 10% by weight of alumina were added to the mixture and water was further added to  
10 give a suitable consistency to the mixture. The resultant mixture was moulded into 3 x 3 mm  
tablets by means of a compression type tableting machine. The tablets were dried at 120°C for 15  
hours and were then immersed in 1 liter of an aqueous solution containing 0.02 gram atoms of  
palladium in the form of palladium nitrate. The thus immersed tablets were removed from the  
15 solution, dried at 120°C for 15 hours and sintered in a stream of air at 700°C for 8 hours to give  
catalytic tablets having, as catalytic components, oxides of chromium, vanadium and palladium. 15

*Example 27*

Alkali-free hydroxides in the form of dried powder prepared by a precipitation method, viz.,  
0.30 gram atoms of chromium in the form of chromium hydroxide, 0.20 gram atoms of bismuth  
20 in the form of bismuth hydroxide and 0.015 gram atoms of palladium in the form of palladium  
hydroxide were mixed together in a mortar. To the mixture were added 1 liter of activated  
alumina powder (200 - 250 mesh per inch) and 0.5 liters of alumina sol containing 10% by weight  
of alumina, and water was further added to the mixture to give a suitable consistency thereto. The  
resultant mixture was moulded into 3 x 3 mm tablets by means of a compression type tableting  
25 machine. The tablets were dried at 120°C for 15 hours and sintered in a stream of air at 700°C for  
8 hours to give catalytic tablets having, as catalytic components, oxides of chromium, bismuth and  
palladium. 25

*Example 28*

Alkali-free hydroxides in the form of dried powder prepared by a precipitation method, viz.,  
0.80 gram atoms of chromium in the form of chromium hydroxide, 0.05 gram atoms of zirconium  
30 in the form of zirconium hydroxide and 0.02 gram atoms of bismuth in the form of bismuth  
hydroxide, and 1 liter of activated alumina powder (200 - 250 mesh (Tyler Standard screen mesh)  
were mixed together in a mortar. To the mixture were added 0.5 liters of alumina sol containing  
10% by weight of alumina, and water was further added to the mixture to give a suitable  
35 consistency thereto. The resultant mixture was moulded into 3 x 3 mm tablets by means of a  
compression type tableting machine. The tablets were immersed in 1 liter of an aqueous solution  
containing 0.02 gram atoms of palladium in the form of palladium nitrate. The thus immersed  
tablets were removed from the solution, dried at 120°C for 15 hours and sintered in a stream of air  
at 700°C for 8 hours to give catalytic tablets having, as catalytic components, oxides of chromium,  
zirconium, bismuth and palladium. 35

*Example 29*

Example 2 was repeated except that a block of a similar alumina-coated monolithic carrier to  
that used in Example 4 was immersed in 3.0 liters of an aqueous solution of a mixture of  
palladium nitrate, chromium nitrate, barium nitrate and zirconyl nitrate wherein the con-  
centrations of palladium ions, chromium ions, barium ions and zirconium ions were 0.018 gram  
45 ions, 1.80 gram ions, 0.29 gram ions and 0.11 gram ions respectively, per liter of the solution.

The resultant monolithic block catalytic composition contained 0.005 gram atoms of  
palladium, 0.50 gram atoms of chromium, 0.08 gram atoms of barium and 0.03 gram atoms of  
zirconium, all in oxide form. 45

*Example 30*

Example 2 was repeated except that a block of a similar alumina-coated monolithic carrier to  
that used in Example 2 was immersed in 3.0 liters of an aqueous solution of a mixture of  
palladium nitrate, chromium nitrate, barium nitrate and aluminium nitrate wherein the  
concentrations of palladium ions, chromium ions, barium ions and aluminium ions were 0.42 gram  
50 ions, 2.1 gram ions, 0.08 gram ions and 0.13 gram ions respectively, per liter of the solution.

The resultant monolithic block catalytic composition contained, derived from the aqueous  
solution, 0.010 gram atoms of palladium, 0.50 gram atoms of chromium, 0.02 gram atoms of  
barium and 0.03 gram atoms of aluminium, all in oxide form. 55

*Example 31*

Example 1 was repeated except that a block of a similar monolithic carrier to that used in  
Example 1 was immersed in 3.0 liters of an aqueous solution of a mixture of palladium nitrate,  
chromium nitrate, magnesium nitrate and bismuth nitrate wherein the concentrations of palladium  
ions, chromium ions, magnesium ions and bismuth ions were 0.077 gram ions, 0.77 gram ions,  
0.051 gram ions and 0.051 gram ions respectively, per liter of the solution. 60

The resultant monolithic block catalytic composition contained, derived from the aqueous  
65 solution, 0.015 gram atoms of palladium, 0.15 gram atoms of chromium, 0.01 gram atoms of

magnesium and 0.01 gram atoms of bismuth, all in oxide form.

*Example 32*

Example 3 was repeated except that 1 liter of a similar carrier to that used in Example 5 was immersed in 1.50 liters of an aqueous solution of a mixture of palladium nitrate, chromium nitrate, magnesium nitrate and vanadium trioxide wherein the concentrations of palladium ions, chromium ions, magnesium ions and vanadium ions were 0.020 gram ions, 2.4 gram ions, 0.20 gram ions and 0.10 gram ions respectively, per liter of the solution.

The resultant catalytic composition contained metal oxides in which 0.010 gram atoms of palladium, 1.2 gram atoms of chromium, 0.10 gram atoms of magnesium and 0.05 gram atoms of vanadium were present in 1 liter of the catalytic composition.

*Example 33*

Example 2 was repeated except that a block of a alumina-coated monolithic carrier similar to that used in Example 4 was immersed in 3.0 liters of an aqueous solution of a mixture of palladium nitrate, chromium nitrate, strontium nitrate and zirconyl nitrate wherein the concentrations of palladium ions, chromium ions, strontium ions and zirconium ions were 0.018 gram ions, 0.72 gram ions, 0.072 gram ions and 0.036 gram ions, respectively, per liter of the solution.

The resultant monolithic block catalytic composition contained 0.005 gram atoms of palladium, 0.20 gram atoms of chromium, 0.02 gram atoms of strontium and 0.01 gram atoms of zirconium all in oxide form.

*Example 34*

Example 1 was repeated except that a block of a similar monolithic carrier to that used in Example 6 was immersed in 3.0 liters of an aqueous solution of a mixture of palladium nitrate, chromium nitrate, strontium nitrate and aluminium nitrate wherein the concentrations of palladium ions, chromium ions, strontium ions and aluminium ions were 0.096 gram ions, 3.8 gram ions, 0.38 gram ions and 0.38 gram ions respectively, per liter of the solution.

The resultant monolithic block catalytic composition contained, derived from the aqueous solution, 0.015 gram atoms of palladium, 0.60 gram atoms of chromium, 0.06 gram atoms of strontium and 0.06 gram atoms of aluminium, all in oxide form.

*Example 35*

Example 2 was repeated except that a block of a similar alumina-coated monolithic carrier to that used in Example 4 was immersed in 3.0 liters of an aqueous solution of a mixture of palladium nitrate, chromium nitrate, barium nitrate, zirconyl nitrate and aluminium nitrate in which the concentrations of palladium ions, chromium ions, barium ions, zirconium ions and aluminium ions were 0.036 gram ions, 1.80 gram ions, 0.18 gram ions, 0.073 gram ions, and 0.18 gram ions respectively, per liter of the solution. The resultant monolithic block catalytic composition contained, derived from the aqueous solution 0.010 gram atoms of palladium, 0.50 gram atoms of chromium, 0.05 gram atoms of barium, 0.02 gram atoms of zirconium and 0.05 gram atoms of aluminium, all in oxide form.

*Example 36*

Example 2 was repeated except that a block of a similar alumina-coated monolithic carrier to that used in Example 2 was immersed in 3.0 liters of an aqueous solution of a mixture of palladium nitrate, chromium nitrate, magnesium nitrate, zirconyl nitrate, and bismuth nitrate wherein the concentrations of palladium ions, chromium ions, magnesium ions, zirconium ions and bismuth ions were 0.042 gram ions, 1.70 gram ions, 0.21 gram ions, 0.085 gram ions and 0.042 gram ions respectively, per liter of the solution.

The resultant block catalytic composition contained, derived from the aqueous solution, 0.010 gram atoms of palladium, 0.40 gram atoms of chromium, 0.05 gram atoms of magnesium, 0.02 gram atoms of zirconium and 0.01 gram atoms of bismuth, all in oxide form.

*Example 37*

Example 1 was repeated except that a block of a similar monolithic carrier to that used in Example 6 was immersed in an aqueous solution of a mixture of palladium nitrate, chromium nitrate, strontium nitrate, bismuth nitrate and vanadium trioxide wherein the concentrations of palladium ions, chromium ions, strontium ions, bismuth ions and vanadium ions were 0.064 gram ions, 1.90 gram ions, 0.13 gram ions, 0.13 gram ions, and 0.13 gram ions respectively, per liter of the solution.

The resultant monolithic block catalytic composition contained, 0.010 gram atoms of palladium, 0.30 gram atoms of chromium, 0.02 gram atoms of strontium, 0.02 gram atoms of bismuth and 0.02 gram atoms of vanadium, all in oxide form.

*Example 38*

Example 2 was repeated except that a block of a similar alumina-coated monolithic carrier to that used in Example 4 was immersed in 3 liters of an aqueous solution of a mixture of palladium nitrate, chromium nitrate, barium nitrate, magnesium nitrate and zirconyl nitrate wherein the concentrations of palladium ions, chromium ions, barium ions, magnesium ions and zirconium ions were 0.036 gram ions, 1.50 gram ions, 0.18 gram ions, 0.036 gram ions, and 0.073 gram ions

respectively, per liter of the solution.

The resultant monolithic block catalytic composition contained, derived from the aqueous solution, 0.010 gram atoms of palladium, 0.40 gram atoms of chromium, 0.05 gram atoms of barium, 0.01 gram atoms of magnesium and 0.02 gram atoms of zirconium, all in oxide form.

5 *Example 39*

Example 2 was repeated except that a block of a similar alumina-coated monolithic carrier to that used in Example 2 was immersed in 3.0 liters of an aqueous solution of a mixture of palladium nitrate, chromium nitrate, barium nitrate, strontium nitrate and aluminium nitrate wherein the concentrations of palladium ions, chromium ions, barium ions, strontium ions and aluminium ions were 0.042 gram ions, 1.70 gram ions, 0.13 gram ions, 0.13 gram ions and 0.21 gram ions respectively, per liter of the solution.

The resultant monolithic block catalytic composition contained, derives from the aqueous solution, 0.010 gram atoms of palladium, 0.40 gram atoms of chromium, 0.03 gram atoms of barium, 0.03 gram atoms of strontium and 0.05 gram atoms of aluminium, all in oxide form.

15 *Example 40*

Example 2 was repeated except that a block of a similar alumina-coated monolithic carrier to that used in Example 4 was immersed in 3.0 liters of an aqueous solution of a mixture of palladium nitrate, chromium nitrate, barium nitrate, strontium nitrate, zirconyl nitrate and aluminium nitrate wherein the concentrations of palladium ions, chromium ions, barium ions, strontium ions, zirconium ions and aluminium ions were 0.036 gram ions, 1.50 gram ions, 0.073 gram ions, 0.073 gram ions, 0.073 gram ions and 0.073 gram ions respectively, per liter of the solution.

The resultant monolithic block catalytic composition contained, derived from the aqueous solution, 0.010 gram atoms of palladium, 0.40 gram atoms of chromium, 0.02 gram atoms of barium, 0.02 gram atoms of strontium, 0.02 gram atoms of zirconium and 0.02 gram atoms of aluminium, all in oxide form.

25 *Example 41*

Example 1 was repeated except that a block of a similar monolithic carrier to that used in Example 1 was immersed in 3 liters of an aqueous solution of a mixture of palladium nitrate, chromium nitrate, barium nitrate, magnesium nitrate, bismuth nitrate and vanadium trioxide wherein the concentrations of palladium ions, chromium ions, barium ions, magnesium ions, bismuth ions and vanadium ions were 0.077 gram ions, 1.90 gram ions, 0.10 gram ions, 0.10 gram ions, 0.10 gram ions and 0.10 gram ions, respectively, per liter of the solution.

The resultant monolithic block catalytic composition contained, derived from the aqueous solution, 0.015 gram atoms of palladium, 0.30 gram atoms of chromium, 0.02 gram atoms of barium, 0.02 gram atoms of magnesium, 0.02 gram atoms of bismuth and 0.02 gram atoms of vanadium, all in oxide form.

35 *Example 42*

Alkali-free hydroxides in the form of dried powder prepared by a precipitation method, viz., 0.20 gram atoms of chromium in the form of chromium hydroxide, 0.005 gram atoms of barium in the form of barium hydroxide and 0.005 gram atoms of zirconium in the form of zirconium hydroxide, and 1 liter of activated alumina powder (200 - 250 mesh (Tyler Standard screen mesh)) were well mixed in a mortar. To the mixture were added 0.5 liters of alumina and water was further added to the mixture to give a suitable consistency thereto. The resultant mixture was moulded into 3 x 3 mm tablets. The tablets were dried at 120°C for 15 hours and immersed in 1 liter of an aqueous solution containing 0.01 gram atoms of palladium in the form of palladium nitrate. The thus immersed tablets were removed from the solution, dried at 120°C for 15 hours, and sintered in a stream of air at 700°C for 8 hours to give catalytic tablets having, as catalytic components, oxides of chromium, barium, zirconium and palladium.

50 *Example 43*

Alkali-free hydroxides in the form of dried powder prepared by a precipitation method, viz., 0.40 gram atoms of chromium in the form of chromium hydroxide, 0.01 gram atoms of magnesium in the form of magnesium hydroxide, 0.01 gram atoms of vanadium in the form of vanadium hydroxide and 0.010 gram atoms of palladium in the form of palladium hydroxide, were mixed together in a mortar. To the mixture were added 1 liter of activated alumina powder (200 - 250 mesh, Tyler Standard screen mesh) and 0.5 liters of alumina sol containing 10% by weight of alumina, and water was further added to the mixture to give a suitable consistency thereto. The resultant mixture was moulded into 3 x 3 mm tablets by means of a compression type tableting machine. The tablets were then dried at 120°C for 15 hours and sintered in a stream of air at 700°C for 8 hours to give catalytic tablets having, as catalytic components, oxides of chromium, magnesium, vanadium and palladium.

60 *Example 44*

Alkali-free hydroxides in the form of dried powder prepared by a precipitation method, viz., 0.80 gram atoms of chromium in the form of chromium hydroxide, 0.03 gram atoms of barium in the form of barium hydroxide, 0.02 gram atoms of strontium in the form of strontium hydroxide,

0.03 gram atoms of zirconium in the form of zirconium hydroxide and 0.02 gram atoms of palladium in the form of palladium hydroxide, were mixed well in a mortar. To the mixture were added 1 liter of activated alumina powder (200 – 250 mesh, Tyler Standard screen mesh) and 0.5 liters of alumina sol containing 10% by weight of alumina, and water was further added to the mixture to give a suitable consistency thereto. The resultant mixture was moulded into 3 x 3 mm tablets by means of a compression type tableting machine. The tablets were then dried at 120°C for 15 hours and sintered in a stream of air at 700°C for 8 hours to give catalytic tablets having, as catalytic components, oxides of chromium, hafnium, strontium, zirconium and palladium.

*Example 45*

Alkali-free hydroxides in the form of dried powder prepared by a precipitation method, viz., 1.20 gram atoms of chromium in the form of chromium hydroxide, 0.02 gram atoms of magnesium in the form of magnesium hydroxide, 0.05 gram atoms of zirconium in the form of zirconium hydroxide and 0.03 gram atoms of bismuth in the form of bismuth hydroxide, and 1 liter of activated alumina powder (200 – 250 mesh, Tyler Standard screen mesh) were mixed well in a mortar. To the mixture were added 0.5 liters of alumina sol containing 10% by weight of alumina, and water was further added to the mixture to give a suitable consistency thereto. The resultant mixture was moulded into 3 x 3 mm tablets by means of a compression type tableting machine. The tablets thus obtained were dried at 120°C for 15 hours and immersed in 1 liter of an aqueous solution containing 0.02 gram atoms of palladium in the form of palladium nitrate. The thus immersed tablets were removed from the solution, dried at 120°C for 15 hours and sintered in a stream of air at 700°C for 8 hours to give catalytic tablets having, as catalytic components, oxides of chromium, magnesium, zirconium, bismuth and palladium.

*Example 46*

Alkali-free hydroxides in the form of dried powder prepared by a precipitation method, viz., 1.50 gram atoms of chromium in the form of chromium hydroxide, 0.03 gram atoms of strontium in the form of strontium hydroxide, 0.03 gram atoms of magnesium in the form of magnesium hydroxide, 0.03 gram atoms of vanadium in the form of vanadium hydroxide and 0.03 gram atoms of bismuth in the form of bismuth hydroxide, and 1 liter of activated alumina powder (200 – 250 mesh, Tyler Standard screen mesh) were mixed well in a mortar. To the mixture were added 0.5 liters of alumina sol containing 10% by weight of alumina, and water was further added to the mixture to give a suitable consistency thereto. The resultant mixture was tableted into 3 x 3 mm tablets by means of a compression type tableting machine. The thus moulded tablets were dried at 120°C for 15 hours, and immersed in 1 liter of an aqueous solution containing 0.02 gram atoms of palladium in the form of palladium nitrate. The thus immersed tablets were removed from the solution, dried at 120°C for 15 hours and sintered in a stream of air at 700°C for 8 hours to give catalytic tablets having, as catalytic components, oxides of chromium, strontium, magnesium, vanadium, bismuth and palladium.

Twelve Comparative Examples are described in the following for the purpose of comparison with the catalytic compositions of the present invention.

*Comparative example 1*

1 liter of a commercially available chi-alumina carrier (6–8 mesh, Tyler Standard screen mesh) was immersed in 1.5 liters of an aqueous solution of a mixture of copper nitrate and chromium nitrate wherein the concentrations of copper ions and chromium ions were 1.0 gram ions and 2.0 gram ions, respectively, per liter of the solution. The thus immersed carrier was removed from the solution, dried at 120°C for 15 hours and sintered in a stream of air at 750°C for 6 hours. The resultant catalytic composition contained 0.5 gram atoms of copper and 1.0 gram atom of chromium both in oxide form per 1 liter of the catalytic composition.

*Comparative example 2*

Comparative Example 1 was repeated except that 1 liter of the same kind of alumina carrier as used in Comparative Example 1 was immersed in 1.50 liters of an aqueous solution of a mixture of copper nitrate, chromium nitrate and palladium nitrate in which the concentrations of copper ions, chromium ions and palladium ions were 1.0 gram ion, 2.0 gram ions, and 0.02 gram ions, respectively, per liter of the solution.

The resultant catalytic composition contained 0.5 gram atoms of copper, 1.0 gram atom of chromium and 0.01 gram atoms of palladium, all in oxide form per 1 liter of the catalytic composition.

*Comparative example 3*

Comparative Example 1 was repeated except that 1 liter of the same kind of alumina carrier as used in Comparative Example 1 was immersed in 1.50 liters of an aqueous solution of a mixture of nickel nitrate and chromium nitrate in which the concentrations of nickel ions and chromium ions both were 1.5 gram ions per liter of the solution.

The resultant catalytic composition contained 0.75 gram atoms of nickel and 0.75 gram atoms of chromium both in oxide form in 1 liter of the catalytic composition.

*Comparative example 4*

Comparative Example 1 was repeated except that 1 liter of the same kind of alumina carrier as

used in Comparative Example 1 was immersed in 1.50 liters of an aqueous solution of a mixture of manganese nitrate, chromium nitrate and copper nitrate wherein the concentrations of manganese ions, chromium ions and copper ions were 1.0 gram ion, 2.0 gram ions, and 1.0 gram ion, respectively, per liter of the solution.

- 5 The resultant catalytic composition contained 0.5 gram atoms of manganese, 1.0 gram atom of chromium and 0.5 gram atom of copper, all in oxide form in 1 liter of the catalytic composition. 5

*Comparative example 5*

Comparative Example 1 was repeated except that 1 liter of the same kind of alumina carrier as used in Comparative Example 1 was immersed in 1.5 liters of an aqueous solution of palladium nitrate in which the concentration of palladium ions was 0.020 gram ions per liter of the solution.

- 10 The resultant catalytic composition contained, when calculated as metal 0.010 gram atoms of palladium in the form of oxide in 1 liter of the catalytic composition. 10

*Comparative example 6*

- 15 A 0.785 liter cordierite block carrier was immersed in 3.0 liters of an aqueous solution of palladium nitrate wherein the concentration of palladium ions was 0.12 gram ions per liter of the solution. The thus immersed carrier was removed from the solution, dried at 120°C for 15 hours and sintered in a stream of air at 800°C for 4 hours. 15

The resultant block catalytic composition contained 0.022 gram atoms of palladium in oxide form.

- 20 *Comparative example 7*

A block of the same kind of monolithic carrier as used in Comparative Example 6 was immersed in a commercially available alumina sol and sintered at 700°C for 3 hours to deposit gamma-alumina thereon. The same process was repeated two times so that the monolithic carrier by a total of 21% by weight of gamma-alumina was finally coated.

- 25 The block of the thus alumina-coated monolithic carrier was immersed in 3.0 liters of an aqueous solution of palladium nitrate wherein the concentration of palladium ions was 0.036 gram ions per liter of the solution. The thus immersed carrier was removed from the solution, dried at 120°C for 15 hours and sintered in a stream of air at 750°C for 6 hours. 25

- 30 The resultant block catalytic composition contained 0.010 gram atoms of palladium in oxide form. 30

*Comparative example 8*

Comparative Example 1 was repeated except that 1 liter of the same kind of alumina carrier as used in Comparative Example 1 was immersed in 1.50 liters of an aqueous solution of a mixture of palladium nitrate and chromium nitrate wherein the concentrations of palladium ions and chromium ions were 0.20 gram ions and 6.2 gram ions, respectively, per liter of the solution.

- 35 The resultant catalytic composition contained 0.010 gram atoms of palladium and 3.1 gram atoms of chromium, both in oxide form in 1 liter of the catalytic composition. 35

*Comparative example 9*

- 40 Comparative Example 1 was repeated except that 1 liter of the same kind of alumina carrier as used in Comparative Example 1 was immersed in 1.5 liters of an aqueous solution of a mixture of palladium nitrate and chromium nitrate wherein the concentrations of palladium ions and chromium ions were 0.020 gram ions and 0.06 gram ions, respectively, per liter of the solution. 40

The resultant catalytic composition contained 0.010 gram atoms of palladium and 0.03 gram atoms of chromium, both in oxide form in 1 liter of the catalytic composition.

- 45 *Comparative example 10*

Comparative Example 1 was repeated except that 1 liter of the same kind of alumina carrier as used in Comparative Example 1 was immersed in 1.50 liters of an aqueous solution of a mixture of palladium nitrate and chromium nitrate wherein the concentrations of palladium ions and chromium ions were 0.0004 gram ions and 2.0 gram ions, respectively, per liter of the solution.

- 50 The resultant catalytic composition contained 0.0002 gram atoms of palladium and 1.0 gram atom of chromium, both in oxide form in 1 liter of the catalytic composition. 50

*Comparative example 11*

- 55 Comparative Example 7 was repeated except that a block of the same kind of a alumina-coated monolithic carrier as used in Comparative Example 7 was immersed in 3.0 liters of an aqueous solution of a mixture of palladium nitrate, chromium nitrate and strontium nitrate wherein the concentrations of palladium ions, chromium ions and strontium ions were 0.042 gram ions, 1.70 gram ions and 1.28 gram ions, respectively, per liter of the solution. 55

The resultant monolithic block catalytic composition contained 0.010 gram atoms of palladium, 0.40 gram atoms of chromium and 0.30 gram atoms of strontium, all in oxide form.

- 60 *Comparative example 12*

- 65 Comparative Example 7 was repeated except that a block of the same kind of alumina-coated monolithic carrier as used in Comparative Example 7 was immersed in 3.0 liters of an aqueous solution of a mixture of palladium nitrate, chromium nitrate and strontium nitrate wherein the concentrations of palladium ions, chromium ions and strontium ions were 0.042 gram ions, 1.70 gram ions, and 0.021 gram ions, respectively, per liter of the solution. 65

The resultant block catalytic composition contained 0.010 gram atoms of palladium, 0.40 gram atoms of chromium and 0.005 gram atoms of strontium, all in oxide form.

Tests were conducted with the catalytic compositions prepared in Examples 1 to 55 and Comparative Examples 1 to 12 to determine the activities thereof. Gases A and B having the compositions indicated in Table 1 below were used as models in the test, wherein the model gas A was used for oxidation reactions while the model gas B was used for reduction reactions. The oxidation and reduction reactions were performed at a space velocity of  $15000 \text{ hr}^{-1}$ . Temperatures of the catalyst bed used were varied in a range of from  $100^\circ\text{C}$  to  $600^\circ\text{C}$  so that a general relation between temperatures and the efficiencies of conversion of propane, carbon monoxide and/or nitrogen monoxide was determined. The efficiency of conversion herein mentioned is intended to mean the proportion in percentage of carbon monoxide, propane or nitrogen monoxide converted into innocuous compounds such as carbon dioxide, nitrogen and water.

Table 1

Constituents		Model gas A	Model gas B
Carbon monoxide,	% by volume	2.0	2.0
Propane,	ppm	500	500
Nitrogen monoxide,	ppm	1000	1000
Carbon dioxide,	% by volume	12.0	12.0
Oxygen,	% by volume	2.5	0
Water vapour,	% by volume	5.0	5.0
Nitrogen,	% by volume	Balance	Balance

The relationship between conversion efficiency and temperatures thus determined is, for example, illustrated by the graph in the accompanying drawing.

Temperatures at which the conversion of carbon monoxide, propane and nitrogen monoxide reached 90% were obtained from the relation indicated by the curve. These temperatures were used for comparison between the catalytic composition of the present invention and the catalytic compositions described in Comparative Examples 1 to 12.

It is, in this instance, apparent that the lower the temperature providing the conversion of 90 per cent, the higher the low-temperature activity of the catalytic composition and vice versa. Thus, the objectives of the present invention will be best met by catalytic compositions exhibiting the 90 per cent conversion at lower temperatures.

Tests were further conducted to evaluate the durabilities of the catalytic compositions prepared in Examples 1 to 55 and Comparative examples 1 to 12. For this purpose, the catalytic compositions to be tested were positioned in a front muffler of an exhaust system of an automotive 4-cycle, 4 cylinder internal combustion engine having a 1600 cc displacement. An output shaft of the engine was connected to a widely used dynamometer to load the engine. The engine was powered by leadless gasoline and cyclically driven through modes of operation including acceleration, normal cruising, deceleration and idling under the conditions analogous to the durability test standards established by AMA (Automobile Manufacturers' Association, United States of America). Secondary air was introduced into the exhaust system upstream of the catalytic composition where the catalytic composition was used for oxidation, while, in the test in which the catalytic composition was used for reduction, secondary air was not supplied to the exhaust system.

The catalytic compositions which had been operated on the tests in which the engine was driven to simulate 5000 km cruising of a motor vehicle were tested for activity with use of the model gases A and B, whereby temperatures providing 90 per cent conversion of the catalytic compositions were determined. The difference between the 90 per cent conversion achieved by the catalytic compositions before and after the durability tests is considered to provide a useful criterion for the evaluation of the durability of the catalytic compositions. Thus, the smaller such difference, the higher the durability of the catalytic composition will be.

The test results are shown in Table 2.

It will be apparent from Table 2 that the catalytic compositions represented by Examples 1 to 55 are vastly superior in low-temperature activity and durability to the prior art catalytic compositions represented by the Comparative Examples 1 to 12.

Table 2

Catalysts	90% Conversion Temperature °C					
	Before Durability Test			After Durability Test		
	CO*	C <sub>3</sub> H <sub>8</sub> *	NO**	CO*	C <sub>3</sub> H <sub>8</sub> *	NO**
Example						
1	340	390	425	375	435	490
2	330	380	415	370	425	475
3	340	385	410	370	430	470
4	335	380	415	365	430	470
5	330	370	410	360	410	460
6	310	355	415	340	385	470
7	330	375	420	370	415	470
8	310	350	410	355	390	465
9	325	370	415	360	410	460
10	320	360	420	360	400	470
11	330	365	410	370	400	460
12	330	370	400	365	405	450
13	330	375	410	375	410	465
14	325	370	410	370	405	455
15	320	370	390	360	410	440
16	360	400	445	390	430	475
17	360	400	445	380	420	465
18	360	405	450	380	440	485
19	360	405	455	380	440	495
20	350	400	455	380	430	490
21	360	405	455	385	430	490
22	355	400	450	370	425	485
23	355	400	455	365	420	480
24	360	410	455	385	440	500
25	355	405	455	375	430	500
26	360	405	450	385	435	495
27	360	400	455	380	430	490
28	360	400	445	375	420	475
29	320	350	405	340	380	435
30	310	360	420	330	380	445
31	320	350	415	340	365	445
32	310	345	410	330	370	440
33	320	350	415	340	370	445
34	320	360	405	335	375	440
35	310	355	410	330	370	435
36	310	350	415	325	375	445
37	325	365	410	330	380	445
38	320	360	405	330	380	435
39	320	360	395	330	380	425
40	320	365	420	335	380	445
41	320	360	410	335	375	445
42	310	350	420	330	370	440
43	315	355	420	325	370	450
44	320	360	415	335	380	445
45	310	350	415	325	370	450
46	310	350	410	330	375	440
Comparative Example						
1	420	480	480	500	570	590
2	410	460	480	480	550	580
3	440	510	460	500	580	560
4	400	460	480	490	540	600
5	420	470	520	490	560	more than 600
6	430	480	540	505	580	"

## WHAT WE CLAIM IS:-

1. A catalytic composition for treating exhaust gases containing carbon monoxide, hydrocarbons and nitrogen oxides, said catalyst composition comprising a carrier and palladium and chromium each being in oxide form, the palladium and chromium being supported by the carrier, the palladium being present in an amount of 0.0003 to 0.1 gram atoms per litre of carrier, the chromium being present in an amount of 0.05 to 3.0 gram atoms per litre of carrier, and the composition being free from copper oxide, the composition further comprising at least one further oxide having catalytic activity and selected from barium, magnesium, strontium, zirconium, bismuth, vanadium and aluminium oxides, the total amount in gram atoms of the metal or metals of said at least further oxide being within the range of 1/50 to 1/2 of the amount in gram atoms of the chromium.
2. A catalytic composition as claimed in claim 1, wherein said carrier is monolithic.
3. A catalytic composition as claimed in claim 2, wherein said carrier is formed from cordierite, beta-spodumene or alpha-alumina.
4. A catalytic composition as claimed in claim 3, further including activated alumina deposited on said cordierite, beta-spodumene or alpha-alumina.
5. A catalytic composition as claimed in claim 4, wherein said activated alumina is gamma-alumina or kappa-alumina.
6. A catalytic composition as claimed in claim 1, wherein said carrier is non-monolithic.
7. A catalytic composition as claimed in claim 6, wherein said carrier is formed from alpha-alumina, gamma-alumina, delta-alumina or chi-alumina.
8. A method of preparing a catalytic composition as claimed in claim 1, the method comprising: forming a carrier in a desired shape; immersing said carrier in a solution containing water-soluble compounds of palladium and chromium, the solution further including at least one salt or other compound of barium, magnesium, strontium, zirconium, bismuth, vanadium and aluminium; drying the carrier and thereafter sintering the carrier at 600 to 900°C.
9. A method as claimed in claim 8, wherein the palladium compound is palladium nitrate, palladium bromide, palladium chloride or palladium sulfate.
10. A method as claimed in claim 8 or 9, wherein said chromium compound is chromium nitrate, chromium acetate, ammonium chromate, ammonium dichromate or chromium trioxide.
11. A method as claimed in any of claims 8 to 10, wherein the barium salt is barium nitrate, barium acetate, barium formate, barium chloride, barium bromide or barium iodide.
12. A method as claimed in any of claims 8 to 11, wherein the magnesium salt is magnesium nitrate, magnesium acetate, magnesium chloride, magnesium bromide or magnesium iodide.
13. A method as claimed in any of claims 8 to 12, wherein the zirconium salt is zirconyl nitrate, zirconium nitrate, zirconium chloride or zirconium iodide.
14. A method as claimed in any of claims 8 to 13, wherein said strontium salt is strontium nitrate, strontium chloride, strontium bromide or strontium iodide.
15. A method as claimed in any of claims 8 to 14, wherein the bismuth compound is bismuth nitrate, bismuth oxide, bismuth chloride or bismuth bromide.
16. A method as claimed in any of claims 8 to 15, wherein the vanadium compound is vanadium chloride, vanadium bromide or vanadium oxide.
17. A method as claimed in any of claims 8 to 16, wherein the aluminium salt is aluminium acetate, aluminium chloride, aluminium bromide or aluminium iodide.
18. A method of preparing a catalytic composition as claimed in claim 1, the method comprising: mixing chromium hydroxide, activated alumina and alumina sol; incorporating at least one further hydroxide selected from hydroxides of barium, magnesium, strontium, zirconium, bismuth and vanadium into the mixture; moulding the mixture incorporating said at least one further hydroxide into a desired shape; immersing the moulding in a solution of a palladium salt selected from palladium nitrate, palladium chloride, palladium bromide and palladium sulfate; and thereafter sintering the moulding at a temperature of 600 to 900°C.
19. A method of preparing a catalytic composition as claimed in claim 1, the method comprising: mixing powders of chromium hydroxide, palladium hydroxide and activated alumina and alumina sol; incorporating at least one further hydroxide selected from hydroxides of barium, magnesium, strontium, zirconium, bismuth and vanadium into the mixture; moulding the resultant mixture incorporating said at least one further hydroxide into a desired shape; drying and sintering the moulding at a temperature of 600 to 900°C.
20. A catalytic composition substantially as hereinbefore described in any of Examples 1 to 46.



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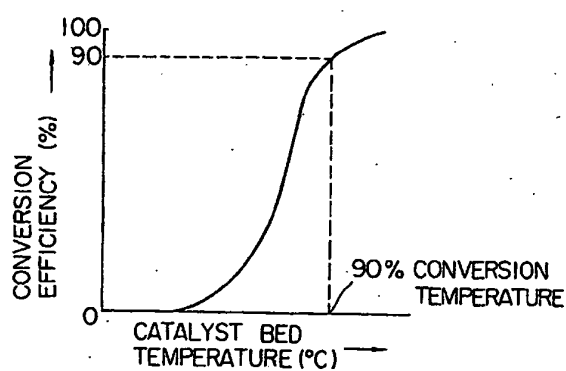
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COMPLETE SPECIFICATION

1 SHEET

*This drawing is a reproduction of  
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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: :  
Fridman, Vladimir, et al. : Group No. 1754  
Serial No.: 10/680,544 ✓ :  
Filing Date: October 7, 2003 ✓ : Examiner: Cam N. Nguyen  
Attorney Docket No.: P-1187 ✓ :  
For: CATALYST FOR DEHYDROGENATION  
OF HYDROCARBONS

Mail Stop Amendment  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, Virginia 22313-1450

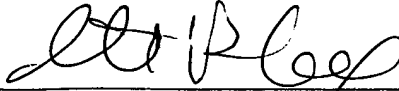
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Respectfully submitted,



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